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Synthesis of pure-silica MTW powder and supported films

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Abstract

High-silica MTW (ZSM-12) was synthesized by a new two-silica method in 8 h in hydroxide medium with tetraethylammonium hydroxide as structure-directing agent. Sodium metasilicate was used as the 1st silica source and shown to induce nucleation/crystallization of MTW in presence of a 2nd silica source such as fumed silica, silica gel and colloidal silica. The synthesis products were characterized by techniques including scanning electron microscopy, X-ray diffraction, magic angle spinning nuclear magnetic resonance, Fourier transform infrared, TGA/DTA, and nitrogen adsorption. The two-silica method was also used successfully to obtain MTW films/membrane on various substrates such as nonporous Al-alloy, porous and nonporous stainless steel and porous α-alumina tubes. © 2002 Elsevier Science Inc. All rights reserved.

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1. Introduction

MTW (ZSM-12) is a high-silica large-pore zeolite with nonintersecting one-dimensional 12-membered ring straight channels [1]. Its framework is highly nonpolar and its channel dimension (5.6×6.0 Å) [1,2] is close to that of medium-pore MFI and MEL zeolites. Except for zeolite MFI and MEL, crystallization of pure-silica zeolites has in general been difficult. Large complex structure-directing agent (SDA) molecules and/or fluoride medium often have to be used, and the crystallization time is long. For example, synthesis of pure-silica MTW has been carried out mainly with large SDA molecules from either hydroxide or fluoride medium, and reported crystallization time for pure-silica MTW varies from several days to several weeks at crystallization temperatures 423–448 K [3–9]. Tsuji et al. [8] succeeded in synthesizing pure-silica MTW within 2.5 days at 438 K in hydroxide medium from synthesis mixture containing 4,4′-trimethylenebis(*N*-benzyl,*N*-methyl-piperidinium) cation and tetraethylorthosilicate (TEOS). This crystallization time appears to be the

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shortest ever reported for pure-silica MTW. Camblor et al. [9] synthesized pure-silica MTW from fluoride medium using a number of different large organic SDA molecules and TEOS. Synthesis from fluoride medium produces highly hydrophobic pure-silica MTW with low defect concentration, but the use of fluoride may limit its practical applications. In addition, the use of large SDA molecules is also of concern because they are usually expensive and their removal requires lengthy calcinations [10].

Synthesis of pure-silica MTW has also been achieved using small simple SDA molecules such as tetraethylammonium (TEA) cations. Toktarev et al. [11] found that the synthesis of MTW with TEA as the SDA was sensitive to the nature of silica source and pure MTW could be obtained only with silica gel while sodium metasilicate produced analcime and other silica sources such as silica sol, fumed silica, and silicic acid produced MFI. In another example, synthesis of pure-silica MTW was achieved in 10 days at 423 K using methyltriethylammonium (MTEA) as SDA [12].

The goal of the present study is to show that highly crystalline pure-silica/high-silica MTW powder can be produced within a short crystallization time (e.g., 8 h) by using a new "two-silica" source strategy with simple SDA molecules (e.g., TEA). There is only one report on the synthesis of zeolites in presence of two-silica source where large mordenite single crystals were obtained from aluminum-containing gel by using sodium silicate and aerosil [13]. The combination of two silica sources—sodium silicate and aerosil—was shown to reduce nucleation and slow down crystallization and thus produce large single crystals. By contrast, in our present study, sodium metasilicate, which does not produce MTW on its own, is shown to promote the nucleation and crystallization of MTW in presence of another silica source (denoted as 2nd silica) such as fumed silica, silica gel, or colloidal silica.

Another goal of the present study is to optimize the synthesis composition and conditions to produce high-silica MTW films on various nonporous and porous substrates. This effort was motivated by the wide range of potential applications of zeolite films [14–17] e.g., separation membranes [14–16], membrane reactors [14,16,18], heat pumps [19], sensors [14,16,20–22], low k dielectrics [23], and corrosion resistant coatings [24]. Preparation of zeolite MTW films has not been reported previously on any supports, and the procedure reported here is fast and highly reproducible.

2. Experimental

2.1. Synthesis of pure-silica MTW powder

To prepare the synthesis mixture, sodium metasilicate (denoted as 1st silica, 44–47 wt.% silica, Aldrich) was first dissolved in de-ionized water. The TEAOH aqueous solution (35 wt.%, Aldrich) was then added and the mixture was stirred at room temperature for 5 min to 24 h. At this time, a 2nd silica source was added and the mixture was further aged at room temperature for 4 h. The 2nd silica source used in this study includes fumed silica (surface area—380 m^2/g, 99.8 wt.% Aldrich), silica gel (35–60 mesh, 99+ wt.%, Aldrich), silicic acid (99.9 wt.%, Aldrich), colloidal silica (LUDOX® AS-30, 30 wt.%, Aldrich) and TEOS (98 wt.%, Aldrich). The synthesis mixture of 15 g was charged into the PTFE vessel of a 45 ml Parr autoclave (4744) before the crystallization was carried out under autogenous pressure in a convection oven. No aluminum source and seed crystals were added to the synthesis mixture.

When the 1st silica—sodium metasilicate—was not used, sodium acetate (sodium acetate trihydrate, 100 wt.%, Fisher Scientific), sodium chloride (99.9 wt.%, Fisher Scientific), or sodium hydroxide (99.99 wt.%, Aldrich) was added to maintain identical Na^+ content of the synthesis mixture. The 2nd silica was added in two doses. The first dose had equivalent amount of silicon as the sodium metasilicate when it was used. After the first dose was added to the sodium source, the mixture was stirred for 4 h at room temperature followed by addition of TEAOH solution and the balance amount of 2nd silica (the second dose).

2.2. Synthesis of MTW films

Siliceous MTW films were obtained by in situ crystallization on stainless steel, tubular α-alumina (pore diameter 0.1 μm), and Al-alloy substrates. No seed crystals were used. Silica gel was always used as the 2nd silica source. The preparation procedure for the synthesis mixture was identical to the one used for the synthesis of MTW powder. Synthesis of film was mainly carried out at 438 K. Substrates were fixed vertically in the synthesis vessel and kept completely immersed in the synthesis mixture (15 g mixture in 45 ml vessel). The stainless steel and Al-alloy substrates were first cleaned with powder Alconox detergent (AlCONOX, INC). Additional treatment for stainless steel substrates include soaking for 30 min in 1 M NaOH and then in 1 M HNO_3 (EM SCIENCE). Finally, all the substrates (stainless steel and Al-alloy) were washed thoroughly with deionized water in an ultrasonic bath for 10 min. For α-alumina tube substrate, it was first cleaned with ethanol followed by washing in hot water. All the substrates were dried at 373 K.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns for as-synthesized zeolite powder as well as films were recorded on a Siemens D-500 diffractometer using CuKα radiation. The morphology of the products was examined by scanning electron microscopy (SEM) at 20 kV, using a Philips XL-30 instrument. Solid-state ^{29}Si magic angle spinning nuclear magnetic resonance (MAS–NMR) spectra were recorded at 9.4 T (^{29}Si operating frequency of 79.36 MHz) on a Varian/Chemagnetics Infinity-Plus NMR spectrometer using a 7.5 mm T3 probe to determine Si environments in as-synthesized sample. The spectra were recorded using a 3.5 μs tip angle (5 μs $\pi/2$) using a relaxation delay of 60 s between the 256 transients while the samples were spun at 5 kHz. High power proton decoupling was performed during the acquisition period. All ^{29}Si spectra were referenced to TMS. Thermal analyses (DTA–TGA) of as-synthesized and calcined pure-silica MTW powder was performed on a SDT 2960 Simultaneous DSC–TGA instrument (TA Instruments) at a heating rate of 5 K/min under a flow of N_2/air (50 ml/min) from room temperature to 1273 K. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Equinox 55 in 375–7500 cm^{-1} range using KBr pellet method. The samples (both as-synthesized and calcined) were mixed with nearly 100 times (by weight) of dry KBr, ground, and dried overnight at 403 K. Nitrogen adsorption–desorption measurements were performed at 77 K on a Micromeritics ASAP 2010. The as-synthesized samples were calcined at 773 K for 12 h under a flow of dry air. Heating rate for the calcination process was 1 K/min. The calcined sample was evacuated overnight at 623 K and 1 μm Hg. Microporosity was determined by *t*-plot method and Horvath–Kawazoe (HK) method was used for the pore size determination.

3. Results and discussion

3.1. Synthesis of pure-silica MTW powder

Table 1 presents a set of experiments carried out for the crystallization of pure-silica MTW. MTW was obtained in presence of sodium metasilicate and fumed silica within 12 h of crystallization (Batch 1). Sodium metasilicate was then taken out of the recipe of the synthesis mixture. Sodium salt (NaAc and NaCl) was added and the amount of 2nd silica was adjusted so that the synthesis mixture has the same $\text{Conc.}_{(OH)^-}$, $\text{Conc.}_{(Na)^+}$, $\text{Conc.}_{(TEA)^+}$ and $\text{Conc.}_{(SiO_2)}$ (Batch 1–3). Addition of sodium chloride (Batch 2) or sodium acetate (Batch 3) favors formation of MFI. Attempt to produce MTW in absence of sodium also failed, and only amorphous product was obtained even after 96 h of hydrothermal treatment (Batch 4). When NaOH was added at a low concentration, only amorphous products were obtained after 48 h of hydrothermal treatment (Batch 5). The amorphous product transformed into cristoballite upon 96 h of hydrothermal treatment (Batch 5). When NaOH was added at a higher concentration (Batch 6 vs. 5), formation of MTW was noticed along with amorphous phase at 48 h and the product eventually transformed into cristoballite (Batch 6). Further increase in the amount of NaOH (as compared to that of Batch 6) failed to produce pure MTW. Pure MTW that is free from amorphous phase or cristoballite was never obtained in

Table 1
Synthesis of MTW powder in presence of fumed silica at 438 K

Batch no.	Gel composition (pH[a])	Crystallization time (h)	Product
1	$1Na_2SiO_3$:$12.47SiO_2$:6.25TEAOH:$131.36H_2O$:0NaOH (12.82)	12–24	MTW
2	$0Na_2SiO_3$:$13.47SiO_2$:6.25TEAOH:$131.36H_2O$:2NaCl (12.57)	24, 96	A + MFI, MFI
3	$0Na_2SiO_3$:$13.47SiO_2$:6.25TEAOH:$131.36H_2O$:2NaAc	24, 96	A + MFI, MFI
4	$0Na_2SiO_3$:(12.47,13.47)SiO_2:6.25TEAOH:$131.36H_2O$:0NaOH (*H*)	24, 96	A
5	$0Na_2SiO_3$:$13.47SiO_2$:6.25TEAOH:$131.36H_2O$:2NaOH (12.94)	48, 96	A, cristoballite
6	$0Na_2SiO_3$:$13.47SiO_2$:6.25TEAOH:$131.36H_2O$:3.1NaOH (13.27)	24, 48, 96	C, A + MTW, cristoballite
7	$1Na_2SiO_3$:$4SiO_2$:6.25TEAOH:$131.36H_2O$:0NaOH (*H*)	24	MFI
8	$1Na_2SiO_3$:$6.25SiO_2$:6.25TEAOH:$131.36H_2O$:0NaOH (*H*)	12–24	MTW
9	$1Na_2SiO_3$:$18SiO_2$:6.25TEAOH:$131.36H_2O$:0NaOH (12.63)	24	MFI + MTW
10	$1.5Na_2SiO_3$:$12.47SiO_2$:6.25TEAOH:$131.36H_2O$:0NaOH (13.14)	12, 24	MTW
11	$0.5Na_2SiO_3$:$12.47SiO_2$:6.25TEAOH:$131.36H_2O$:0NaOH (12.96)	48, 96	MFI

A–amorphous, C–clear solution, no solid material produced. *H* indicates value close to upper limit of pH meter (≅14).
[a] pH values of initial gel before crystallization.

presence of NaOH and fumed silica for all the compositions attempted.

From the above discussion, it is clear that the addition of sodium metasilicate promotes nucleation/crystallization of MTW. Failure to produce pure MTW in presence of sodium acetate, sodium chloride, or sodium hydroxide (Batch 2, 3, 5) indicates that Na^+ associated with acetate, chloride or hydroxide may behave differently from that associated with metasilicate species during crystallization of MTW. Goepper et al. [5] showed that the addition of sodium (either $NaNO_3$ or NaOH) facilitates the crystallization of pure-silica MTW in presence of fumed silica and 4,4′-trimethylenebis(dimethylpiperidinium) hydroxide. Pure-silica MTW was obtained within 7 days of crystallization at 423 K with sodium as compared to 84 days without it [5]. Such promoting role of sodium was observed in our synthesis only in combination with metasilicate species. No such effect was observed when equivalent amount of sodium was present with chloride, acetate or hydroxide ions (Batch 2, 3, 5).

To examine the effect of (2nd silica)/(1st silica) molar ratio on product selectivity, systematic changes of the ratio were made by changing the amount of either SiO_2 (2nd silica) (Batch 7–9) or Na_2SiO_3 (1st silica, Batch 10, 11). It appears that the (2nd silica)/(1st silica) ratio is important in determining the crystallization of MTW. Pure MTW was obtained at $6.25 \leqslant$ (2nd silica)/(1st silica) $\leqslant 14$. Attempts to synthesize MTW using sodium metasilicate or fumed silica individually both failed and this is consistent with the results of Ref. [11]. It thus appears that a small amount of sodium metasilicate is necessary to promote the formation of MTW in presence of fumed silica. Crystallization time remained unchanged when (2nd silica)/(1st silica) was reduced to 6.25 (Batch 8 vs. 1). However, yield of the product [Yield (wt.%) = (amount of silica in the product/amount of silica in the gel) $\times$ 100] was decreased (typical yield is about 50 wt.%).

The effect of 2nd silica on the overall activity of the synthesis mixture was also studied (Table 2). Fumed silica was substituted by silica gel (Batch 12), TEOS (Batch 13), silicic acid (Batch 14) and colloidal silica (Batch 15). MTW was obtained in presence of sodium metasilicate with silica gel and colloidal silica as the 2nd silica source. In contrast, TEOS and silicic acid failed to produce MTW in the presence of sodium metasilicate. Efforts to synthesize MTW with TEOS, silicic acid, or colloidal silica as the only silica source also failed and this is consistent with the findings of Ref. [11]. A combination of sodium metasilicate and fumed silica/silica gel/colloidal silica enabled the formation of MTW within a short crystallization time. As mentioned earlier, Toktarev et al. [11] found that the synthesis of MTW is extremely sensitive to the nature of the silica source. It was shown that using single-silica source MTW can only be pro-

Table 2
Effect of second silica source on the synthesis of MTW at 438 K

Batch no.	Batch composition (pH[a])	Crystallization time (h)	2nd silica source	Product
1	$1Na_2SiO_3$:$12.47SiO_2$:6.25TEAOH:$131.36H_2O$ (12.82)	12–24	Fumed silica	MTW
12	$1Na_2SiO_3$:$12.47SiO_2$:6.25TEAOH:$131.36H_2O$ (12.88)	5–24	Silica gel	MTW
13	$1Na_2SiO_3$:$12.47SiO_2$:6.25TEAOH:$131.36H_2O$ (13.68)	24, 96	Tetraethylorthosilicate	C, A
14	$1Na_2SiO_3$:$12.47SiO_2$:6.25TEAOH:$131.36H_2O$ (12.82)	24, 48	Silicic acid	A, A + MFI
15	$1Na_2SiO_3$:$12.47SiO_2$:6.25TEAOH:$131.36H_2O$	24	Colloidal silica	MTW
16	3.1NaOH:$13.47SiO_2$:6.25TEAOH:$131.36H_2O$ (13.03)	15–36	Silica gel	MTW

A–amorphous, C–clear solution, no solid material produced.
[a] pH values of initial gel before the crystallization.

duced from silica gel while fumed silica, colloidal silica, silicic acid and TEOS all failed. Our study shows that the addition of sodium metasilicate is able to overcome the inability of fumed silica and colloidal silica to produce MTW, but not that of TEOS and silicic acid. It is noted when an excess amount of sodium hydroxide was used, silica gel alone could produce pure MTW (Batch 16).

Fig. 1 shows the progress of crystallization with time for syntheses in presence of silica gel and fumed silica. Intensity of the strongest XRD peak (310 plane of MTW) was plotted against the corresponding crystallization time. The opaque hydrogel turned completely transparent within 2 h of crystallization. For synthesis with silica gel and sodium metasilicate, crystallization product started appearing within 5 h and clear solution became turbid at this time for synthesis. Crystallization was completed within 10 h at 438 K. Carrying out the synthesis at higher temperature could shorten crystallization time further and completely crystalline MTW was obtained within 8 h at 448 K. In the case of synthesis in presence of fumed silica and sodium metasilicate, formation of MTW was noticed within 12 h of crystallization while complete crystallization took nearly 16 h at 438 K. Silica gel appears to be the best silica source for crystallization of MTW and the shortest crystallization time is 8 h at 448 K. To the best of our knowledge, this is the shortest ever reported for this zeolite.

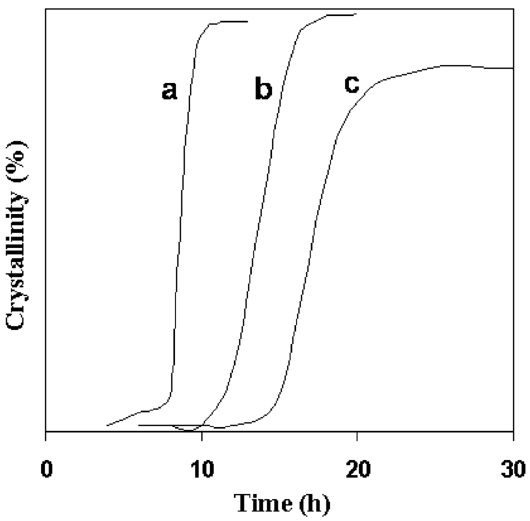

Fig. 1. Progress in crystallization with time for (a) sodium metasilicate + silica gel (Batch 12), (b) sodium metasilicate + fumed silica (Batch 1) and (c) sodium hydroxide + silica gel (Batch 16).

Fig. 2 shows SEM picture of the crystallites obtained in presence of sodium metasilicate and silica gel (Fig. 2a), sodium metasilicate and fumed silica (Fig. 2b), sodium hydroxide and silica gel (Fig. 2c), respectively. It is clearly seen that the crystallites obtained from sodium hydroxide and silica gel were 2–4 times larger than that obtained from sodium metasilicate and silica gel. The result shows higher nucleation in presence of sodium metasilicate as compared to sodium hydroxide. Furthermore, the yield for synthesis from sodium metasilicate and silica gel is twice that from sodium hydroxide and silica gel. The crystallites from sodium metasilicate and fumed silica are slightly larger than from sodium metasilicate and

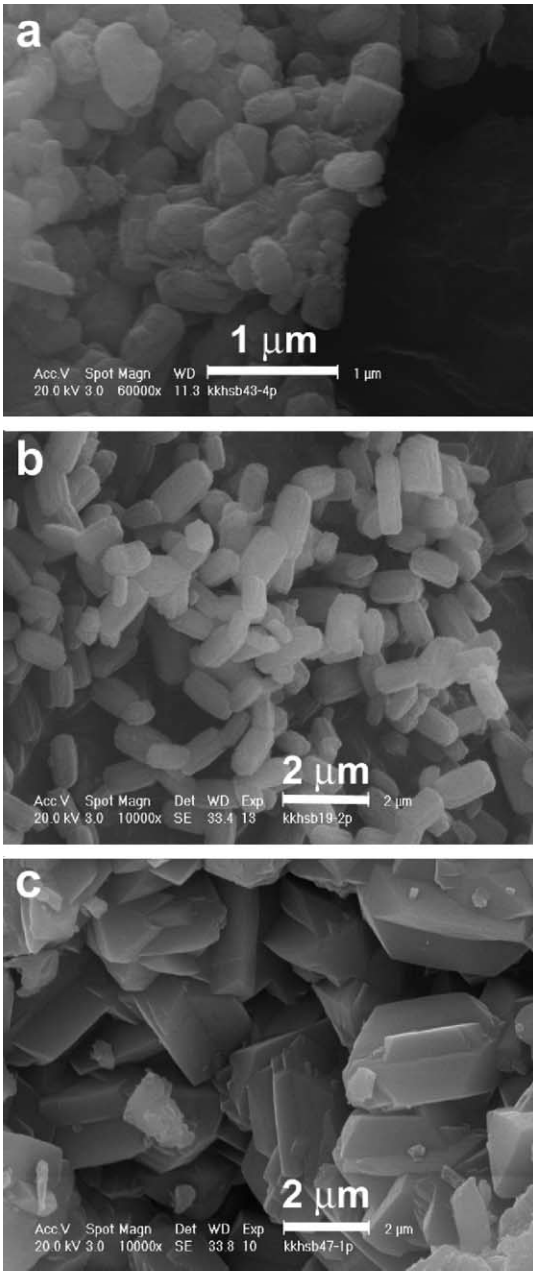

Fig. 2. SEM images of as-synthesized pure-silica MTW crystals obtained from (a) sodium metasilicate + silica gel (Batch 12), (b) sodium metasilicate + fumed silica (Batch 1) and (c) sodium hydroxide + silica gel (Batch 16).

silica gel, again indicating higher nucleation for sodium metasilicate and silica gel. Difference in crystal size and yield confirms that the addition of sodium metasilicate facilitates the crystallization by providing a suitable environment for the nucleation of MTW. In addition, the nucleation of MTW was not only controlled by sodium metasilicate but by the combination of sodium metasilicate and the 2nd silica source.

3.2. Characterization of pure silica MTW powder

XRD pattern of as-synthesized all-silica MTW powder obtained in presence of sodium metasilicate and silica gel is shown in Fig. 3. High crystallinity and purity of the sample is evident. MTW obtained from sodium metasilicate and fumed silica/colloidal silica also produced similar diffraction pattern.

Fig. 4 shows ^{29}Si MAS–NMR spectra of the as-synthesized MTW. There are three peaks at around −97.6, −104.4, and −113.0 ppm for MTW obtained from silica gel and sodium metasilicate (Fig. 4a) and two peaks at around −104.4 and −113.0 ppm for MTW from fumed silica and sodium metasilicate (Fig. 4b). The NMR spectrum for MTW from silica gel and NaOH (Fig. 4c) is similar to that of MTW from silica gel and sodium metasilicate. ^{27}Al NMR (spectra not shown) was also carried out on all of three samples. No Al peak was observed for MTW with fumed silica as the 2nd silica source while extremely weak peaks were found for MTW with silica gel as the 2nd silica source. The Al is likely from silica gel as a

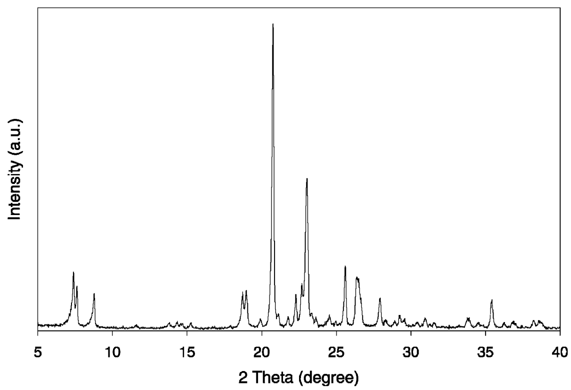

Fig. 3. XRD pattern of pure-silica MTW powder from sodium metasilicate + silica gel.

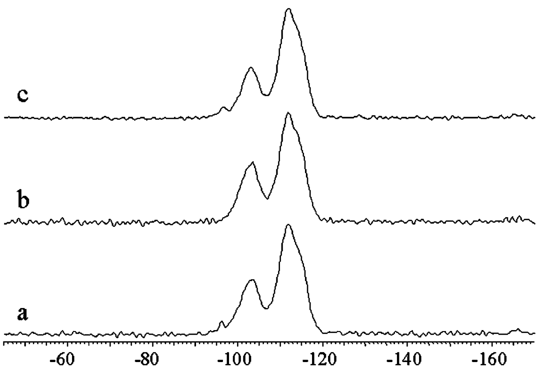

Fig. 4. ^{29}Si MAS–NMR spectra of as-synthesized MTW obtained in presence of (a) sodium metasilicate + silica gel, (b) sodium metasilicate + fumed silica, and (c) sodium hydroxide + silica gel.

minor impurity. Therefore peaks at −113.0, −104, and −97.6 ppm are assigned to SiQ^4, SiQ^3 and SiQ^2 (1OH & 1Al), respectively. The presence of Si (1OH & 1Al) in MTW from silica gel is consistent with our TG data shown below.

Fig. 5 shows TG spectra of as-synthesized samples obtained under a flow of N_2 at the rate of 50 ml/min and heating rate 5 K/min. Removal of organic species occurs at about 600 K for product obtained in presence of sodium metasilicate and silica gel (Fig. 5a). DTG spectrum shows a one-step removal of TEA while MTW containing significant amount Al usually shows multiple-step template removal [11] with the major exothermic peak centered at 643 K. The removal of template occurs at much lower temperature from the product obtained in presence of fumed silica and sodium metasilicate as compared to that in presence of silica gel and sodium metasilicate (Fig. 5b). TG spectrum of MTW obtained in presence of sodium hydroxide and silica gel was identical to that obtained in presence of sodium metasilicate and silica gel. The decrease of removal temperature of the organic species indicates less interaction of the organic species with the framework obtained in presence of fumed silica and sodium metasilicate. ^{29}Si MAS–NMR spectra showed presence of Si (1-OH & 1Al) environment in MTW obtained from silica gel and this is likely to be responsible for the change in TG spectrum. Very

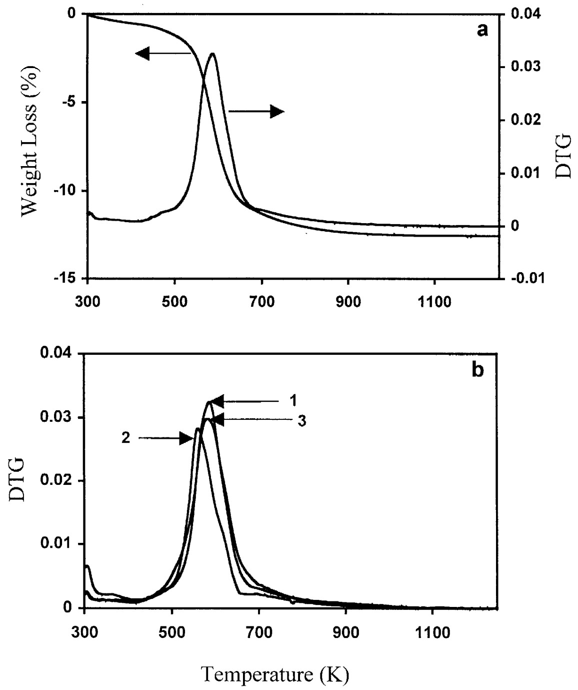

Fig. 5. (a) TG/DTG spectra of as-synthesized high-silica MTW powder synthesized from sodium metasilicate + silica gel (Batch 12), (b) DTG spectra of high-silica MTW powder synthesized from (1) sodium metasilicate + silica gel (Batch 12), (2) sodium metasilicate + fumed silica (Batch 1), and (3) sodium hydroxide + silica gel (Batch 16).

similar results were obtained while the spectra were recorded under air. Facile and complete removal of organic species from the framework was achieved irrespective of the atmosphere of TG experiments e.g., inert N_2 atmosphere or under air. Complete removal of organic species was confirmed by the TG analysis of the calcined sample and N_2 adsorption studies.

FT-IR (Fig. 6) and XRD of as-synthesized and calcined MTW samples show no loss of crystallinity during calcinations. High crystallinity of calcined samples was further confirmed by N_2 adsorption–desorption studies (Fig. 7). Na-containing, calcined, pure-silica MTW has surface area of 270 m^2/g and microporore volume of 0.11 cm^3/g as determined by *t*-plot method, and this value is in excellent agreement with that reported for Al-MTW samples [25,26].

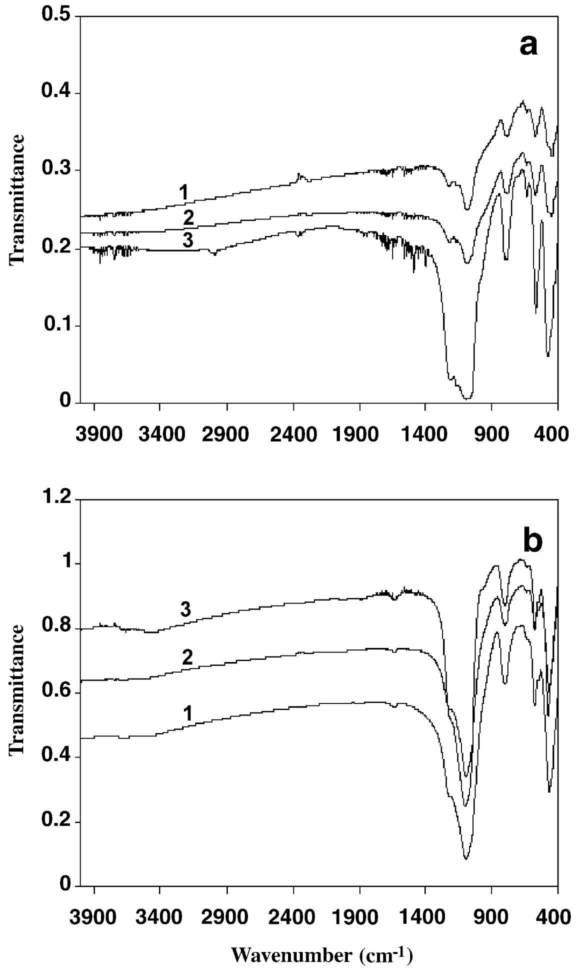

Fig. 6. FTIR spectra of (a) as-synthesized MTW obtained with (1) sodium metasilicate and silica gel (Batch 12), (2) sodium metasilicate and fumed silica (Batch 1), (3) silica gel only (Batch 16), and (b) calcined MTW obtained with (1) sodium metasilicate and silica gel (Batch 12), (2) sodium metasilicate and fumed silica (Batch 1), and (3) silica gel only (Batch 16).

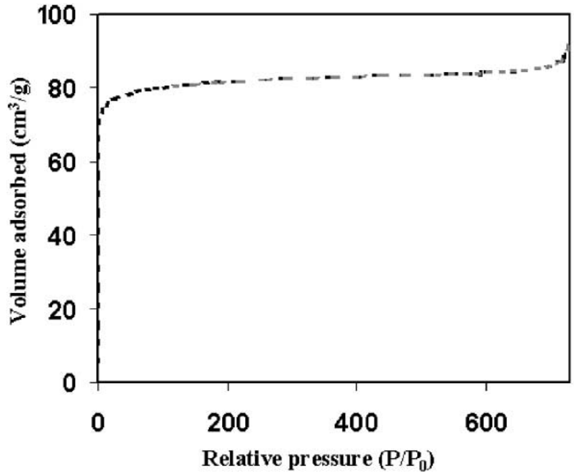

Fig. 7. N_2 adsorption isotherm of calcined pure-silica MTW synthesized from sodium metasilicate + silica gel (Batch 16).

3.3. Synthesis and characterization of siliceous MTW film

Table 3 shows a set of experiments to produce MTW films on various substrates. Pure MTW films were obtained on stainless steel within 16 h of crystallization from a synthesis mixture with molar composition $1Na_2SiO_3/6.25TEAOH/12.47SiO_2/131.36H_2O$ (Batch 17) and the film remained stable under highly alkaline synthesis medium up to 72 h. Prolonged crystallization for 4–5 days resulted in in situ disappearance of MTW film from the substrate, and pure cristoballite was obtained in the bulk at this time (Batch 18). Formation of spherical cristoballite crystals (compared to the elongated MTW crystals) was noticed in the film after 90 h of crystallization. The amount of cristoballite increases (XRD and SEM) with crystallization time. SEM images (Fig. 8) of the film obtained after 90 h of crystallization indicate a solid state transformation of elongated MTW crystals to spherical cristoballite crystals followed by the disappearance of the spherical crystals under the combined effect of gravity and surface properties of the newly formed crystals. Pure MTW films could be obtained on stainless steel within 16 h of crystallization in a wide range of synthesis compositions (Batch 17, 19, 20). It has been mentioned earlier that pure MTW powder could be obtained in the bulk within 10 h of crystallization under identical experimental conditions. Film formation, however, is influenced by the presence of the substrate, and does not entirely parallel the bulk crystallization. Only poorly crystalline MTW film was obtained after 10 h of crystallization. Moreover, the film was only weakly adhered to the substrate and could be removed during washing by ultrasonication. The films obtained 16 h onwards were strongly adhered to the

Table 3
Synthesis of MTW coating/membranes on various substrates in presence of silica gel and sodium metasilicate at 438 K

Batch No.	Batch composition (pH[a])	Crystallization time	Substrate	Film
17	$1Na_2SiO_3$:$12.47SiO_2$:6.25TEAOH:$131.36H_2O$ (12.88)	16–72 h	SS 304[b]	MTW
18	$1Na_2SiO_3$:$12.47SiO_2$:6.25TEAOH:$131.36H_2O$	96 h	SS 304	None
19	$1Na_2SiO_3$:$6SiO_2$:6.25TEAOH:$131.4H_2O$ (*H*)	16 h	SS 304	MTW
20	$1Na_2SiO_3$:$6SiO_2$:3TEAOH:$131.4H_2O$ (12.42)	16 h	SS 304	MTW
21	$1Na_2SiO_3$:$6SiO_2$:2TEAOH:(105– 210)H_2O	24 h, 36 h	α-alumina, Al-6061-T4, Al-2024-T3	MTW

H indicates value close to the upper limit of pH meter (≅14).
[a] pH values of initial gel before the crystallization.
[b] SS—stainless steel.

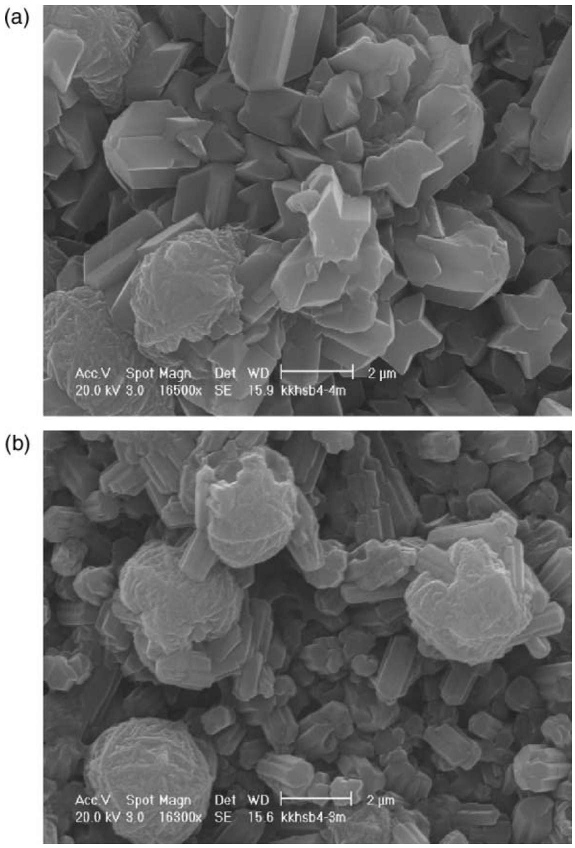

Fig. 8. Formation of cristoballite (spherical crystals) on siliceous MTW films containing elongated MTW crystals on stainless steel substrates after 90 h of crystallization at 438 K. The images (a) and (b) were photographed on the same film at different locations.

substrate and could not be detached by ultrasonication or by polishing with 0.3 μm α-Al_2O_3 suspension using a Buehler polisher. The stainless steel substrate used was polished on one side. MTW films were observed on both sides and the film on the rough side is 2–3 times thicker.

It was observed that a lower (2nd silica)/(1st silica) ratio produces less bulk product and well inter-grown, continuous (visually and under SEM) MTW films on stainless steel (Batch 19). However, pure MTW could not be obtained at (2nd silica)/(1st silica) ratio less than 6. Increasing water content of the gel also could reduce the amount of bulk product. However, dilution causes drop in crystallization rate. On the other hand, reduction of TEAOH content of the gel (from Batch 19 to Batch 20) reduces thickness of the film. Thin film (thickness < 1 μm) of MTW was obtained on stainless steel substrates from a gel with molar composition $1Na_2SiO_3$/3TEAOH/$6SiO_2$/$131.4H_2O$ (Batch 20). Crystallization time remained unchanged while changing the amount of TEAOH and/or 2nd silica in the gel. Further reduction of TEAOH content of the gel enabled formation of pure MTW on aluminum containing substrates in a short crystallization time (Batch 21). Syntheses of pure MTW on aluminum containing substrates were found to be extremely sensitive to the hydroxyl ion concentration. A higher hydroxyl ion concentration (as compared to that of Batch 21) causes impurities of MFI on α-alumina and beta and/or MFI on Al-alloy substrates. Similar films were formed on both sides of the aluminum alloy substrates.

Fig. 9 shows XRD patterns of as-synthesized MTW films on various substrates. Partially oriented

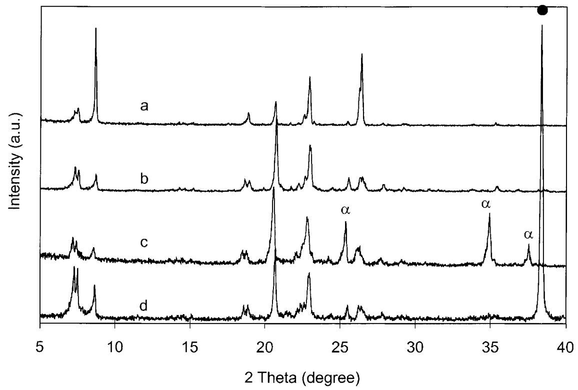

Fig. 9. XRD pattern of MTW films on (a) stainless steel 304 (at 413 K), (b) stainless steel 304 (thin film, 438 K), (c) α-alumina ('α' indicates reflections due to α-alumina), (d) Al-alloy Al-2024-T3 ('●' indicates reflection of Al-alloy substrate).

thick film of MTW was obtained on polished stainless substrates at 413 K after 6 days of crystallization (Fig. 9a). The crystals were found to be oriented with their *b* axis parallel to the substrate. The one-dimensional channels of MTW are parallel to the *b* axis [1,3]. No preferential orientation was achieved on porous steel substrates as well as Al-containing substrates.

Fig. 10 shows SEM top-view images of as-synthesized MTW films on various substrates. The corresponding cross-sectional images are presented in Fig. 11. The cross-section of the films is marked with a white vertical bar. The films appear densely packed with good intergrowth and variable roughness. Surface roughness of the films could be reduced by polishing with 0.3 μm α-Al_2O_3 suspension using a Buehler polisher. Polishing experiments reveals that the film is mechanically strong and adhered well to the substrates. Cross-sectional image shows (Fig. 11a) formation of thin MTW film (thickness < 1 μm) on stainless steel substrates under low alkaline conditions. The thickness of MTW film on α-alumina (Fig. 11b) was found to be around 3.5–4 μm whereas the film on Al-alloy (Fig. 11c) was nearly 2 μm thick. Cross-sectional images clearly shows strong interaction of the crystallites with the substrate. The film appeared to be deeply rooted inside the substrates.

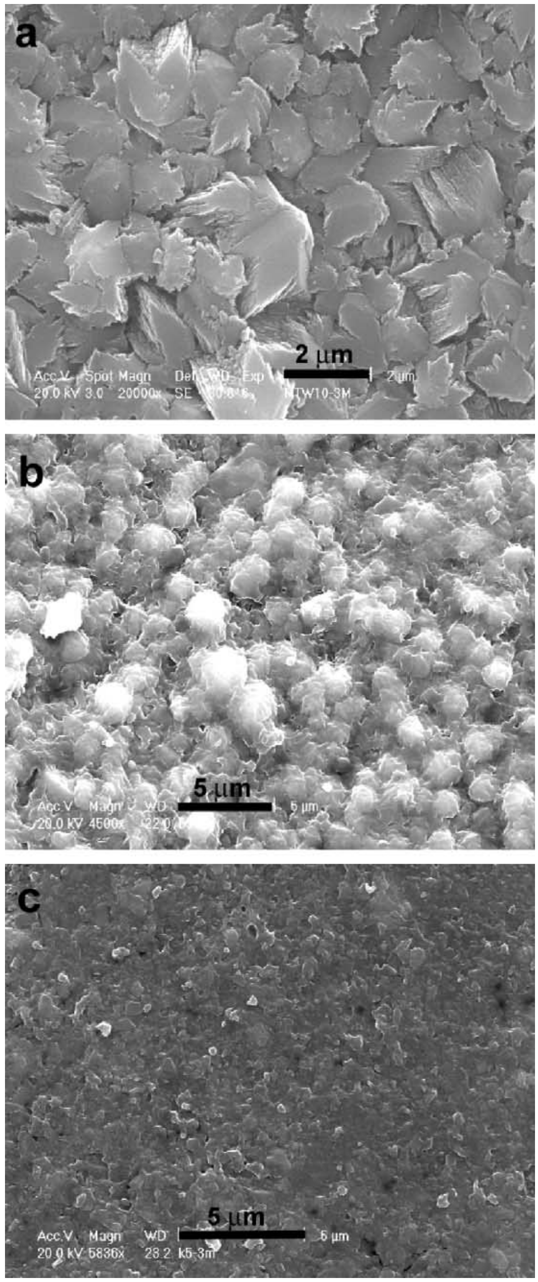

Fig. 10. Surface SEM images of as-synthesized MTW films on (a) stainless steel substrate, (b) α-alumina, and (c) Al-alloy.

Recently corrosion resistant MFI coating has been synthesized on nonporous Al-alloy [24]. Al-alloy coated with a compact layer of MFI was shown to have extremely low polarization current

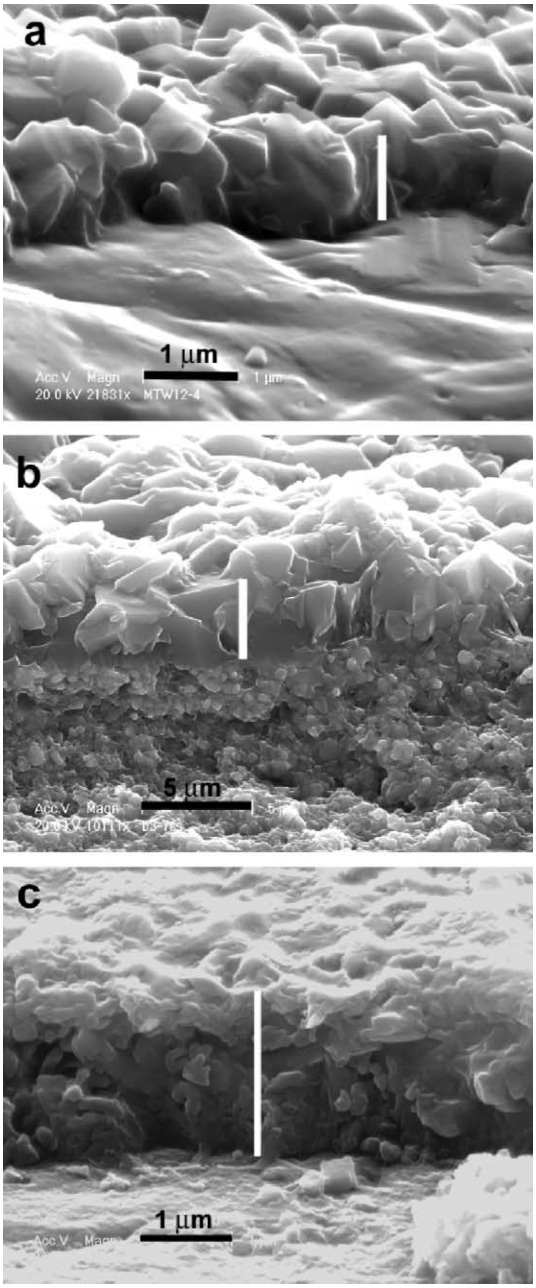

Fig. 11. Cross-sectional SEM images of as-synthesized MTW films on (a) stainless steel (thin film), (b) α-alumina, and (c) Al-alloy.

in highly corrosive media. Measurement of polarization current of the substrates coated with MTW films in highly corrosive medium was used to determine the quality of the as-synthesized MTW films on metal alloy substrates. Polarization test indicates formation of highly corrosion resistant MTW film on stainless steel and Al-alloy substrates. Detailed studies on polarization test on MTW coated stainless steel and Al-alloy substrates are presented elsewhere [27]. On the other hand, gas permeation experiment, which is crucial to determine the quality of MTW membranes on porous substrates, is under investigation. It will be highly desirable to synthesize MTW films with *b* axis perpendicular to the substrate for applications such as membrane, sensor, etc. however, no such film has yet been obtained.

4. Conclusion

A new two-silica synthesis method has been developed that can produce pure-silica MTW within a short crystallization time (e.g., 8 h) with TEA as the SDA. The addition of sodium metasilicate was shown to induce nucleation and crystallization of MTW from fumed silica and colloidal silica that is otherwise incapable of producing MTW. On the other hand, yield and nucleation rate was doubled in presence of sodium metasilicate while silica gel was used as second silica source. The organic species can be removed easily from the as-synthesized product by calcination at 773 K. Further, a synthesis composition $1Na_2SiO_3/(6.3–2)TEAOH/(6–12.5)SiO_2/(105–210)H_2O$ with two-silica source has been developed that can form MTW films within a short crystallization time on porous and nonporous steel, aluminum alloy, and alumina ceramic substrates.

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